SOME OBSERVATIONS ON PROTON MAGNETIC RESONANCE IN HYDROGEN-BONDED SYSTEMS

BY

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UPPSALA 1957

ALMQVIST & WIKSELLS BOKTRYCKERI AB

Some Observations on Proton Magnetic Resonance in Hydrogen-bonded Systems

INAUGURAL DISSERTATION

BY

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BY DUE PERMISSION OF THE FACULTY
OF SCIENCE OF THE UNIVERSITY OF UPPSALA,
TO BE PUBLICLY DISCUSSED
IN THE LECTURE HALL OF THE INSTITUTE OF PHYSICS,
ON MAY 24TH, 1957, AT 10 A.M., FOR THE
DEGREE OF 'FILOSOFIE DOKTOR'

UPPSALA 1957
ALMQVIST & WIKSELLS BOKTRYCKERI AB

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The "chemical shift" effect in the nuclear magnetic resonance phenomenon which was originally suggested by Professor Kai Siegbahn and Docent Gunnar Lindström during their experiments on the magnetic moment determination of some light nuclei at Nobel Institute of Physics forms the basis of the investigations described in the communications presented here. The experimental equipment needed in these studies is, however, not the same as that used in magnetic moment determinations. This may be seen from the description of the equipment given in our communication entitled "A spectrometer for high resolution nuclear magnetic resonance experiments". As explained in that communication, one of the essential requirements of the technique of the high resolution nuclear magnetic resonance (n.m.r.) is high stability of the magnetic field for which a permanent magnet is usually preferred. Our systematic procedures for "line narrowing" were started when the construction of the big permanent magnet at this institute was nearly completed in August, 1954, although some earlier preliminary attempts were made with an electromagnet.

Investigations concerning "chemical shift" belong to the domain of molecular phenomenona, although the method of n.m.r. by which it is observed is of specific nuclear origin. The "chemical shift" effect is an entirely physical effect due to the interaction of the magnetic field on the motions of the electrons in the molecule. The origin of these "chemical shifts" in n.m.r. phenomena and their diverse features have been adequately discussed in our communications IV and VII.

Studies of the "internal chemical shift" in molecules depending upon the immediate electronic environment around the nucleus is of great value in (i) determination of molecular configurations of organic compounds in liquid phases, (ii) studies of any specific interactions between atoms and molecules as in hydrogen bonding and (iii) studies of processes concerning the formation of new molecules e.g. in chemical reactions. These three features in the molecular domain form the main subject matter of our high resolution n.m.r. studies and some of the observations are new, as may be seen from our communications presented here.

The idea regarding the diamagnetic shielding and internal chemical shift of protons in relation to hydrogen bonding and molecular association in some organic compounds outlined in communication I has been elaborately discussed in communica-

tion VII, where more experimental observations are presented. These experiments on so-called H-bond shift show convincingly the specific interaction between the molecules involving the protons in the hydrogen bond. The experimental observations also show the difference in the type of hydrogen bonding in carboxylic acids and alcohols, which we mentioned earlier in communication I in regard to the difference in behaviour of H-bond shift between alcohols and acetic acid in carbon tetrachloride solution. The cubic nature of the proton chemical shift curve in acetic acid–water system may be qualitatively explained as due to the hydrogen bond formation between acetic acid and water molecules. The explanation seems to be corroborated from infra-red and Raman spectroscopic studies. The suggestion of pressure dependence of H-bond shift made from the cubic nature of the proton chemical shift curve in acetic acid–water system has helped us to interpret some observation of Ogg on chemical shift in ammonia, as discussed in communication III.

The H-bond shift in propionic acid described in communication VII justifies the suggestion of the dimeric structure of propionic acid, as stated from chemical shift observation in propionic acid–water system described in communication II. In propionic acid the electron-coupled spin-spin interaction parameter between protons in methyl (CH_3) and methylene (CH_2) groups is determined and found to be the same as in ethyl alcohol molecule, although the internal chemical shift for the two groups in those two molecules are different. This observation justifies the well accepted view that the electron-coupled spin-spin interaction is dependent only on the covalent part of the bond between the two adjacent chemical groups.

In communication VI we have shown with experiments how the chemical shift in n.m.r. phenomenon can be applied to study the kinetics of the hydrolysis of acetic anhydride. The n.m.r. results were in fair agreement with those found by an actual chemical experiment during the major part of the reaction but towards the end of which there was some divergence. The cause of this divergence was partly attributed to dimerisation of acetic acid, the final product of the reaction, thus keeping the picture of acetic acid molecules consistent with our views outlined in communication I. Some other physical causes of the divergence associated with the method of observation such as the possible effect of a magnetic field on chemical reactions are discussed in communication VII. The effect of temperature and molecular-complex-forming solvent on the hydrolysis of acetic anhydride was also studied by the method and is described in communication VII. The method is applicable to study reactions in concentrated solutions where many other methods are not accessible. The n.m.r. method has been extended to study the reaction between methyl alcohol and acetic anhydride and is described in communication VII. This experiment brings out some more details in the n.m.r. signals than the earlier experiment.

The proton resonance in the acetylacetone molecule has been studied in some detail in regard to its molecular configurations in keto and enol forms which differ in respect to the position of a hydrogen atom. In communication V, while de-

scribing an experiment on the determination of the equilibrium constant between the two forms, some physical causes due to which differences in the equilibrium constant value from chemical and n.m.r. methods may arise are also discussed. In communication VII, the observation of unusually low diamagnetic shelding of OH protons in acetylacetone and the intra-molecular hydrogen bonding is discussed and experimental observations of H-bond shift are given. An experiment to determine the unimolecular transformation of the two forms of the molecule is described and the experimental findings are discussed in the light of Gutowsky and Saika's theory of chemical shift.

In communication IV, the apparatus and the experimental techniques of high resolution n.m.r. are described. While Bloch's method of "line narrowing" has been used, the technique of detecting nuclear signals is the nuclear resonance absorption method employing a single-coil twin-T radio frequency bridge which, unlike the Purcell bridge, admits of simple adjustment of the proper balance for observation of the resonance signals.

Acknowledgements

The present work has been carried out at the Nobel Institute of Physics, Stockholm. I wish to express my profound gratitude to Professor Manne Siegbahn, Director of the Institute, for his kindness in giving me the opportunity of working in the Nobel Institute and the hospitality so kindly shown to me during my stay in Sweden. I shall never forget Professor Siegbahn's magnanimous help in my humble academic pursuit.

I wish to express my sincere thanks to Professor Kai Siegbahn, Professor of Physics of the University of Uppsala, for his kind interest in our work on nuclear magnetic resonance.

I wish to express my sincere thanks to Docent Gunnar Lindström for his valuable advice, encouragement and interest in our work.

I wish to thank heartily all members of the staff of this institute whose friendly co-operation was beneficial to our work.

Lastly on this occasion I gratefully recall those days when I was associated with the Calcutta University where my work on nuclear magnetic resonance was started, and I take this opportunity to record my sincere thanks to Professor S. K. Mitra and Professor S. N. Bose of my mother institution and to Professor D. M. Bose of the Bose Research Institute at Calcutta, India.

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